



MTI Technical Paper

**McDermott
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Research and
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Division**

***Realistic
Solutions to
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Problems***

Full-Scale Testing of Mercury Control for Wet FGD Systems

G.T. Amrhein
G.A. Kudlac
D.M. Madden
McDermott Technology, Inc.
Alliance, Ohio

Presented at the
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on Coal Utilization and Fuel Systems

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G.T. Amrhein, G.A. Kudlac, D.M. Yurchison
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Abstract

Babcock & Wilcox and McDermott Technology, Inc (B&W/MTI) recently completed the field test portion of a full-scale demonstration of mercury control for wet flue gas desulfurization (wet FGD) systems. Data reduction and chemical analyses are still on going. Project participants include the U. S. Department of Energy's (DOE) National Energy Technology Laboratory (NETL), the Ohio Coal Development Office (OCDO) within the Ohio Department of Development, Michigan South Central Power Agency (MSCPA), and Cinergy. The host sites for the field tests were MSCPA's 55 MW_e Endicott Station in Litchfield, Michigan and Cinergy's 1300 MW_e Zimmer Station in Moscow, Ohio.

B&W/MTI's technology employs the addition of a proprietary reagent to a wet scrubber system. In pilot-scale testing at B&W's 10 MW_e Clean Environment Development Facility, this approach was shown to potentially increase mercury capture in a wet scrubbing system to 90% or greater. Benefits of the B&W/MTI technology include:

- Cost-effective mercury control
- Co-pollutant control
- No adverse effects on scrubber operation or performance
- No impact on by-product disposal or usage

This paper addresses the design/test plans and initial results for the full-scale utility demonstrations.

Introduction

More than a decade ago B&W and MTI had the vision to focus on mercury control for the electric power industry. Over the years, several pilot-scale project efforts have identified approaches to improve mercury control for wet scrubbing systems. In October 2000, a project entitled "*Full-Scale Testing of Enhanced Mercury Control for Wet FGD Systems*" was begun. The ultimate goal of the project is to commercialize methods for the control of mercury in coal-fired electric utilities equipped with wet FGD.

A wide range of mercury removals has been reported for wet scrubbers in coal applications appear with a number of factors contributing to this variability. For example, significant differences in the mercury content of U.S. coals result in a wide range of mercury concentrations in the flue gas from the boiler. In addition, the form, or species, of mercury (elemental or oxidized) in the flue gas is thought to affect wet FGD system mercury removal efficiency. Mercury speciation in the flue gas may also be influenced by coal type, with sub-bituminous coals often producing a higher relative proportion of elemental mercury than bituminous coals. Finally, the wet scrubber configuration, liquid-to-gas ratio, and slurry chemistry may also impact the mercury emissions control.

Wet FGD systems are currently installed on about 25% of the coal-fired utility generating capacity in the U.S., representing about 15% of the number of coal-fired units. Depending on the effect of the operating parameters mentioned above, wet FGD systems can provide the basis for cost-effective, near term mercury control with a proven history of commercial operation. For boilers already equipped with wet FGD systems, the incremental cost of any vapor phase mercury removal achieved is minimal. To be widely accepted and implemented, technical approaches that improve mercury removal performance for wet FGD systems should also have low incremental costs and have little or no impact on operation and SO₂ removal performance.

Benefits of the B&W/MTI Enhanced Wet FGD Mercury Removal Process

The primary and obvious benefit from the B&W/MTI enhanced wet FGD mercury removal process is the reduction of mercury emissions from coal-fired utility power plants. Other benefits include:

Cost-effective. Based on preliminary economic analyses that have been completed, the B&W/MTI enhanced wet FGD mercury removal technology has been shown to be significantly more cost-effective than activated carbon for the same level of removal. Preliminary annual levelized costs were estimated for 90% removal of mercury in a 500 MW_e plant. Assuming activated carbon costs between \$0.50 and \$0.55 per pound, the annual levelized cost is estimated at \$17,500/lb mercury removed for the activated carbon system. For B&W/MTI's system the annual levelized cost is about \$950/lb mercury removed. It should be noted that activated carbon costs have been estimated in the literature to be as high as \$70,000/lb mercury removed depending on the amount of carbon needed and the material's cost. Therefore, it is expected that mercury removal using B&W/MTI's technology will cost less than 10% of that using activated carbon.

B&W/MTI's technology is cost-effective because:

- *Use of existing equipment.* Little additional equipment will be required for implementation.
- *Low capital cost.* Because the technology requires little additional equipment and only minor modification

of existing equipment for installation, capital costs are extremely low.

- *Low operating cost.* Currently, the most promising technology for mercury control alone is assumed to be activated carbon injection. Unfortunately, sorbent costs are very high for carbon injection. The reagent used in B&W/MTI's technology is low in cost and readily available for application of the technology.

Co-Pollutant Control. Multiple pollutant analysis was recently documented in a report prepared by the U. S. EPA entitled, "Analysis of Emissions Reduction Options for the Electric Power Industry." The study looked at options to lower air emissions of sulfur dioxide (SO₂), for fine particulate control, mercury, and carbon dioxide (CO₂). The basic conclusion to the analysis was that an integrated, multi-pollutant approach to the control of these emissions could offer significant cost savings relative to a piecemeal approach. That conclusion applies directly to the use of wet FGD systems rather than activated carbon for mercury control since wet scrubbers capture multiple pollutants while activated carbon systems target only mercury.

Compatible with Current Emissions Control Technologies. The approach is ideally suited to wet FGD systems, since it utilizes existing equipment and provides mercury control with a proven history of commercial operation. The technology can be easily applied to both existing and new wet FGD systems. All testing to date indicates that this approach has no adverse effects on wet scrubber performance or operation.

Technical Approach

The goal of this project was to conduct full-scale, long-term, field-testing of B&W/MTI's enhanced wet FGD mercury removal technology to obtain mercury removal performance and cost data. The technology utilizes very small amounts of a proprietary reagent for increased mercury removal efficiency. Field-testing was completed at two commercial coal-fired utilities with wet FGD systems: 1) MSCPA's 55 MW_e Endicott Station and 2) Cinergy's 1300 MW_e Zimmer Station. Testing was conducted at these two locations because of the large differences in size and wet scrubber chemistry. Endicott employs a limestone,

forced oxidation (LSFO) wet FGD system, whereas Zimmer uses Thiosorbic® Lime (magnesium enhanced lime) and *ex situ* oxidation. Both locations burn Ohio high-sulfur bituminous coal.

MSCPA Endicott Station. Figure 1 shows MSCPA's Endicott Station. The plant burns 140,000 tons of Ohio coal per year. The air pollution control equipment includes a cold side, dry electrostatic precipitator (ESP) followed by a wet scrubber. The ESP has a flyash removal efficiency greater than 98%. A single B&W LSFO wet FGD absorber is used for SO₂ control. The limestone slurry preparation system consists of a crusher, tower mill and classifier. The system typically operates at 92% SO₂ removal. Primary dewatering is achieved with a single thickener, with two rotary drum vacuum filters for secondary dewatering. Approximately 28,000 tons/year of gypsum are produced and sold as byproducts.

Cinergy Zimmer Station. Figure 2 shows Cinergy's Zimmer Station. The plant burns 3.5 million tons of Ohio coal per year. The air pollution control equipment includes two ESP and six B&W wet FGD scrubbers. The precipitators have a flyash removal efficiency of 99.9%. The wet FGD system at Zimmer uses Thiosorbic® lime as the reagent that is prepared in a system consisting of ball mills, classifiers and slurry storage tanks. Some oxidation occurs naturally in the wet scrubbers, but the unit is currently using an *ex situ* oxidation system. SO₂ removal efficiency is typically controlled at 92%, but the unit is capable of 95% removal efficiency. Two methods of dewatering/solids production are available. The wet FGD system was originally equipped and operated with thickeners for primary dewatering, and belt vacuum filters for secondary dewatering. With this method the dewatered filter cake is fixed and stabilized with the addition of flyash and lime in a pug mill, then landfilled. Recently, the system was upgraded to produce



Fig. 1 MSCPA Endicott Station.



Fig. 2 Cinergy Zimmer Station.

wallboard-quality gypsum. An *ex situ* forced oxidation system was added along with hydroclones for primary dewatering. The upgrade allows for the production of up to 900,000 tons/year of gypsum. Table 1 compares the characteristics of the two test locations.

Field Operation Phases. Figure 3 shows the project schedule and illustrates the testing phases necessary to prove the commercial success of the B&W/MTI enhanced wet FGD mercury removal process. Field

operation began at the Endicott Station. The phases of operation at the Endicott Station were as follows:

- Parametric testing to define the optimal operating parameters for the process.
- Two weeks of verification testing to verify the performance of the process with the selected operating conditions.
- Four months of long-term operation to continue the verification of the amount of mercury removal achieved and to prove that there were no long-term effects on SO₂ removal, materials of construction, or byproduct utilization.

After completing field operation at the Endicott Station, the B&W/MTI enhanced mercury removal system was moved to the Zimmer Station for testing. Field operation at the Zimmer Station included:

- Two weeks of verification testing to verify the performance of the process with the selected operating conditions.

Table 1 Test Location Characteristics Comparison.

	MSCPA Endicott Station	Cinergy Zimmer Station
Electricity Generation	55 MW _e	1300 MW _e
Number of Wet Scrubber Modules	1	6
Wet Scrubber Reagent	Limestone	Thiosorbic® Lime
Wet Scrubber Oxidation Method	<i>In situ</i> Forced Oxidation	Natural Oxidation
Wet Scrubber Liquid-to-gas Ratio	78 gal/1000 acf	21 gal/1000 acf
Slurry pH	5.4 – 5.6	5.8 – 6.0
Inlet SO ₂ Concentration	3600 ppm	3300 ppm
Gypsum Use	Cement	Wallboard

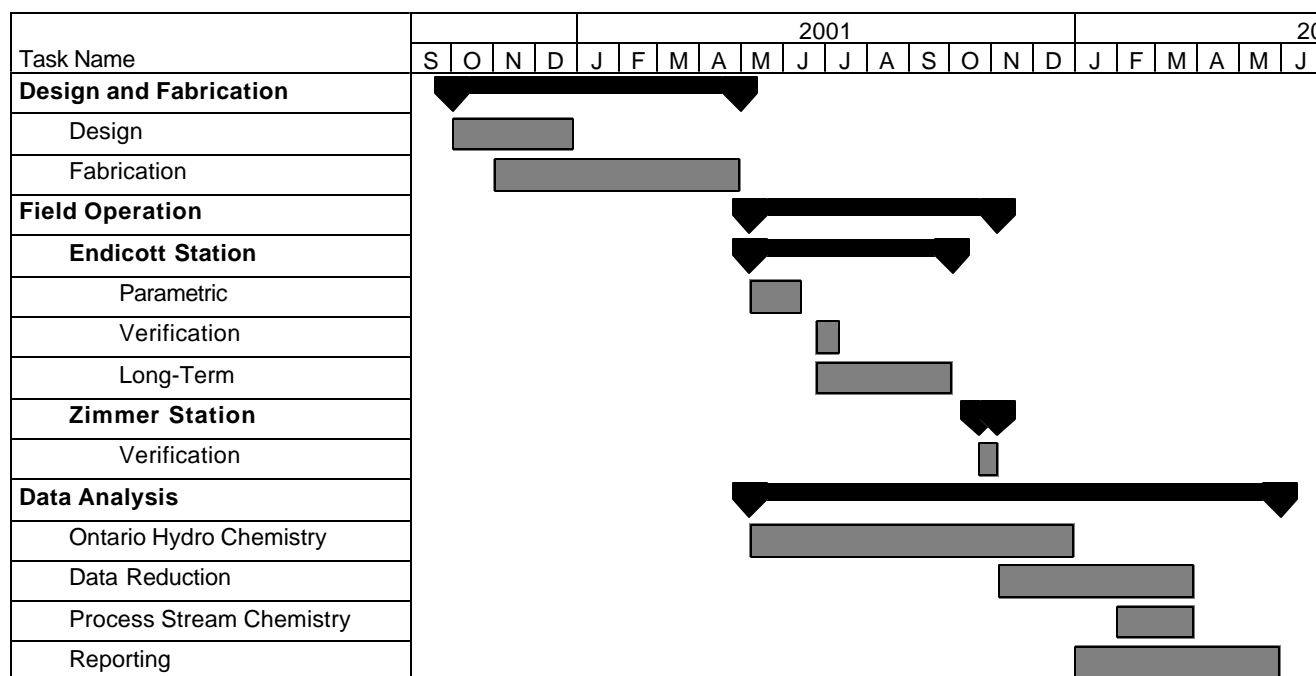


Fig. 3 Project schedule.

To facilitate minimal construction and set-up at each plant site, a mobile equipment skid was fabricated to connect to the existing wet scrubber systems. The equipment skid is shown in Figure 4.

Ontario Hydro Method (O-H) measurements were made to determine total mercury and mercury speciation. The O-H method applies to determination of particulate and gaseous mercury emissions from industrial, utility and municipal sources. Particulate and gaseous emissions are isokinetically withdrawn

from a source and collected on either a quartz fiber filter, in potassium chloride (KCl) solutions, in acidic peroxide, or in acidic potassium permanganate (KMnO_4) solutions. Oxidized mercury is collected in the KCl impingers, and elemental mercury is collected in the peroxide and potassium permanganate impingers. During analysis, the mercury collected in the impingers is reduced to elemental mercury, aerated from the solution, and measured by cold vapor atomic absorption spectroscopy (CVAAS). For all sampling, strict stationary source emissions testing quality assurance procedures, as specified by the O-H method, were used to control all potential sources of sample contamination.

The results presented in this report reflect the mercury removal across the wet scrubber only and do not include the mercury removal that may occur before the scrubber. Sample train and equipment preparation and recovery took place in a fully equipped, mobile laboratory trailer shown in Figures 5 and 6. The specific sampling locations for the project were the wet scrubber inlet and wet scrubber outlet (stack). A PS Analytical on-line mercury analyzer was also used during testing. The on-line analyzer is shown in Figure 7.



Fig. 4 Reagent injection skid.



Fig. 5 Laboratory trailer.

O-H measurements were made at the inlet and outlet of the wet scrubber system at both Endicott and Zimmer resulting in mercury removal across the wet scrubber. Figures 8 through 11 show the locations and sampling set-ups for the O-H measurements. Figures 8 and 9 are the Endicott wet scrubber inlet and outlet (stack) sampling locations. Figures 10 and 11 are the Zimmer wet scrubber system inlet and outlet (stack) sampling locations. At Zimmer, measurements were made around the entire wet scrubber system, not individual modules.

The process streams that were collected for chemical analysis included coal, ESP ash, wet scrubber slurry, limestone, lime, and waste solids (gypsum). Sample analysis is currently on going. It is important in the determination of where the mercury is coming into the system and what streams and in what amount the mercury is leaving the system. Figures 12 and 13 show the gypsum produced at the Endicott and Zimmer Stations.



Fig. 6 Sample recovery in the laboratory trailer.



Fig. 7 PS analytical on-line mercury analyzer.

Preliminary Results

Before the field demonstration, there were several projects at MTI's 10 MW_e CEDF that investigated the effect of various mercury control technologies. *The Mercury Control for Coal-Fired Utilities Program* resulted in one of the most promising technologies. Pilot-scale testing results are shown in Figure 14. Each pair of bars represents the O-H results for the



Fig. 8 Endicott, wet scrubber inlet sampling location.



Fig. 9 Endicott, wet scrubber outlet sampling location.

flue gas at the inlet and outlet of the scrubber. Each bar consists of two segments that show the oxidized and elemental portions of the flue gas. The bars represent an average of three O-H tests at each location.

The first set of bars represent the baseline case and show that most of the mercury at the scrubber inlet was present in the oxidized form as is typical for Ohio coals. More importantly, however, the outlet bar shows that while most of the oxidized mercury was removed in the scrubber, a significant amount was reduced to elemental mercury within the scrubber and discharged into the flue gas. This effect occurred only when using an ESP for particulate capture upstream from the scrubber.

The remaining pairs of bars represent tests at different reagent injection rates and show that the reagent



Fig. 10 Zimmer, wet scrubber system inlet sampling location.

prevents the reduction of oxidized mercury to elemental mercury and increases scrubber mercury removal. Mercury removal across the scrubber was as high as 87%. Chemical analyses of the scrubber slurry showed that the resulting mercury compound is insoluble and the solids are thermally stable to at least 140°C (140°C is the temperature required to drive off the required waters of hydration in the wall board process).

Figure 15 shows the O-H results from full-scale tests performed at Endicott. Again, the bar pairs show the flue gas mercury concentration at the scrubber inlet and outlet, and each bar shows the proportion of oxidized and elemental mercury. The bars represent an average of three O-H tests at each location. Compared to the pilot data shown in Figure 14, these full-scale tests were conducted at a normalized reagent flow of about 0.33.



Fig. 11 Zimmer, wet scrubber system outlet sampling location.



Fig. 12 Endicott, gypsum sample taken from drum filter.



Fig. 13 Zimmer gypsum product.

There are two sets of baseline data for Endicott taken about a month apart. Like the pilot test, this data shows that most of the mercury at the scrubber inlet was oxidized. However, while Test 1 shows that a significant amount of the oxidized mercury was reduced to elemental mercury, like the pilot test, Test 5 does not. The reason for this difference is not known and is still being investigated. All tests with

reagent injection, completed over 4-months of continuous operation, show no appreciable increase in elemental mercury across the scrubber, and the average scrubber removal was 79%. The overall mercury removal (ESP and wet FGD) will be higher for these tests but will not be calculated until after coal analyses are completed.

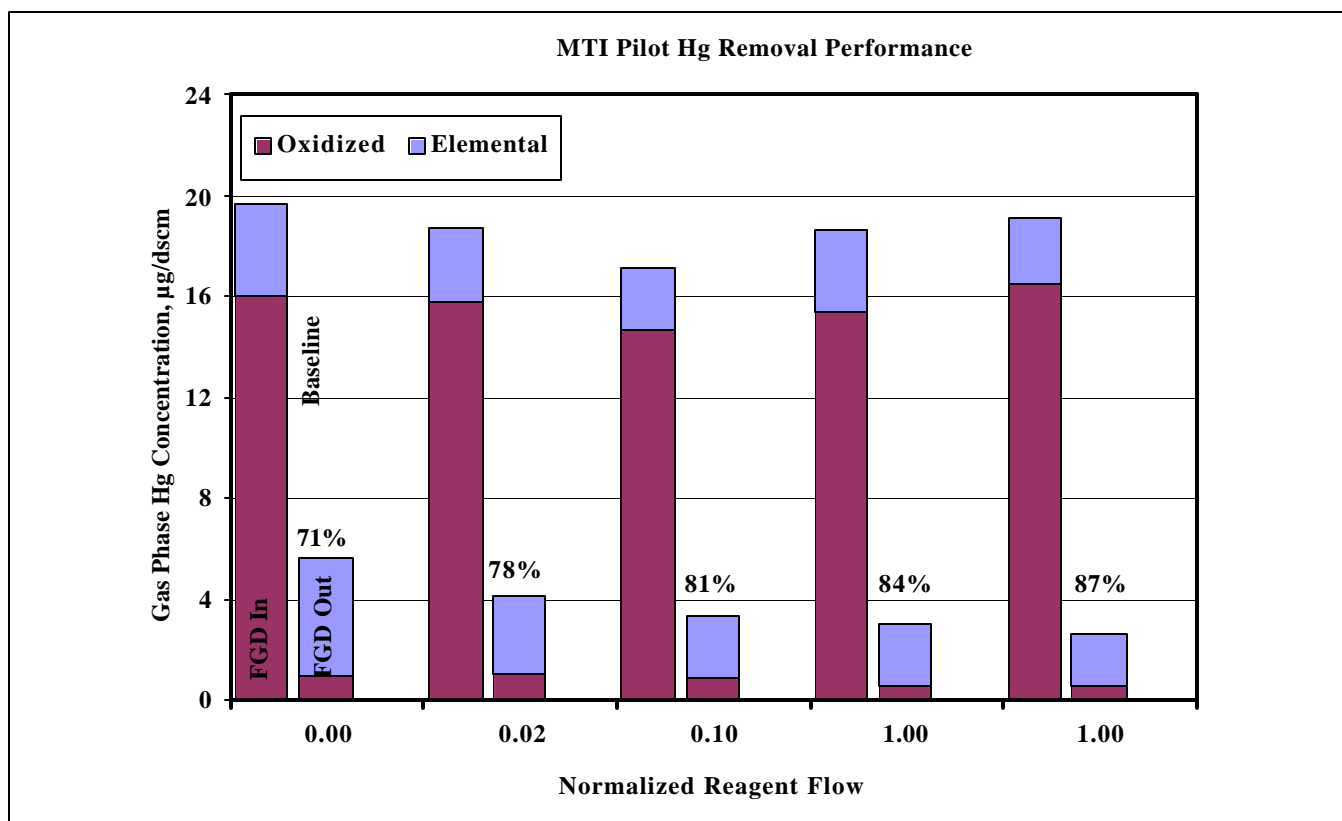


Fig. 14 Mercury control results at MTI (ESP, LSFO wet FGD)

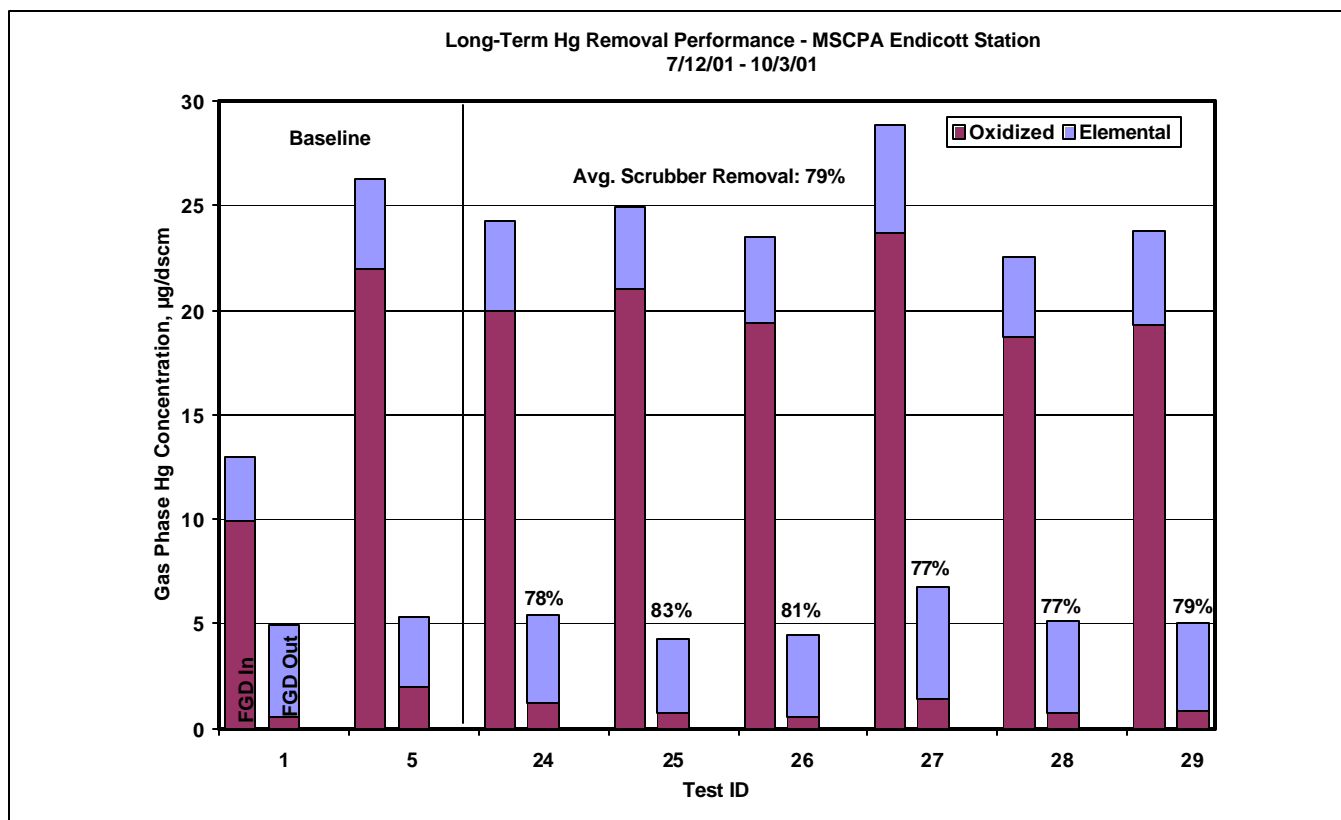


Fig. 15 Mercury Control Results at Endicott (ESP, LSFO wet FGD).

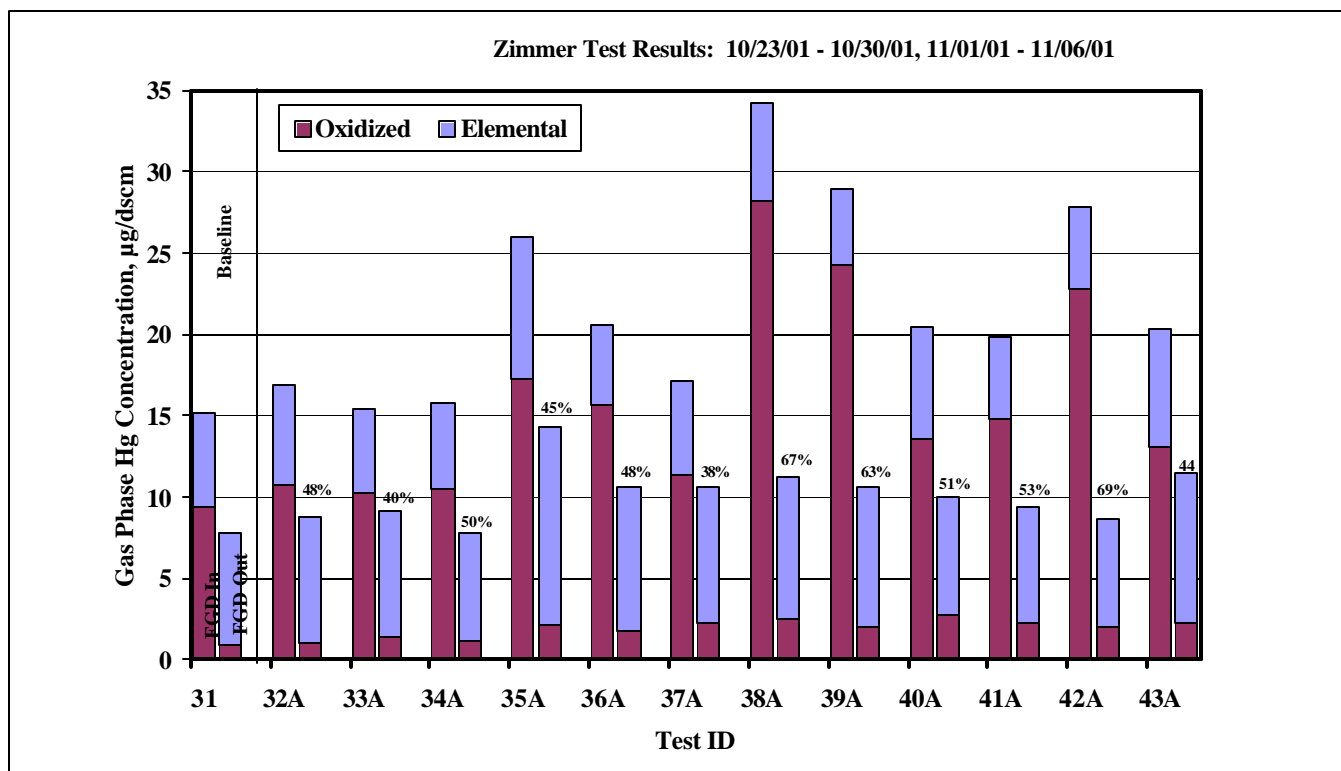


Fig. 16 Mercury Control Results at Zimmer (ESP, Thiosorbic® Lime wet FGD, *Ex situ* Oxidation).

Figure 16 shows the O-H results from full-scale tests performed at Zimmer. The bars represent an average of three O-H tests at each location for the baseline and one set of O-H data for the reagent tests. Compared to the pilot data, the tests with reagent were conducted at a normalized reagent flow of about 0.33 as at Endicott.

Unlike the other two sites, the bars representing the inlet mercury concentration at Zimmer generally show a much larger percentage of elemental mercury. An increase in mercury across the scrubber was again observed in the baseline test. However, in this case, the reagent appeared to have no significant effect on mercury removal. For every test, the amount of elemental mercury measured at the outlet was higher than the inlet. One possible explanation for this is that Thiosorbic® lime systems contain a much higher sulfite ($\text{SO}_3^{=}$) concentration. At the low levels of reagent used for these tests, the high level of sulfite may

overwhelm the reagent and contribute to the reduction step¹. Chemical analyses of the coal and slurry samples from Zimmer are ongoing, so a comparison with the pilot test and Endicott is not yet possible. The average scrubber mercury removal at Zimmer was 45%. The graph also shows that significant variations in inlet mercury concentration can occur in a 24-hour period. Also, the elemental portion of the flue gas does not change as much as the oxidized portion.

Figure 17 is a comparison of scrubber inlet and outlet elemental mercury concentrations for the pilot, for the verification and long term tests at Endicott, and for the Zimmer tests. The normalized reagent flow for the pilot tests was 1.0 and the field tests were at 0.33. Baseline data are shown as open symbols. The data illustrates an increase in elemental mercury across the scrubber for the baseline tests (data above the 45° line), and how the reagent prevents this effect and may even promote elemental mercury removal (data

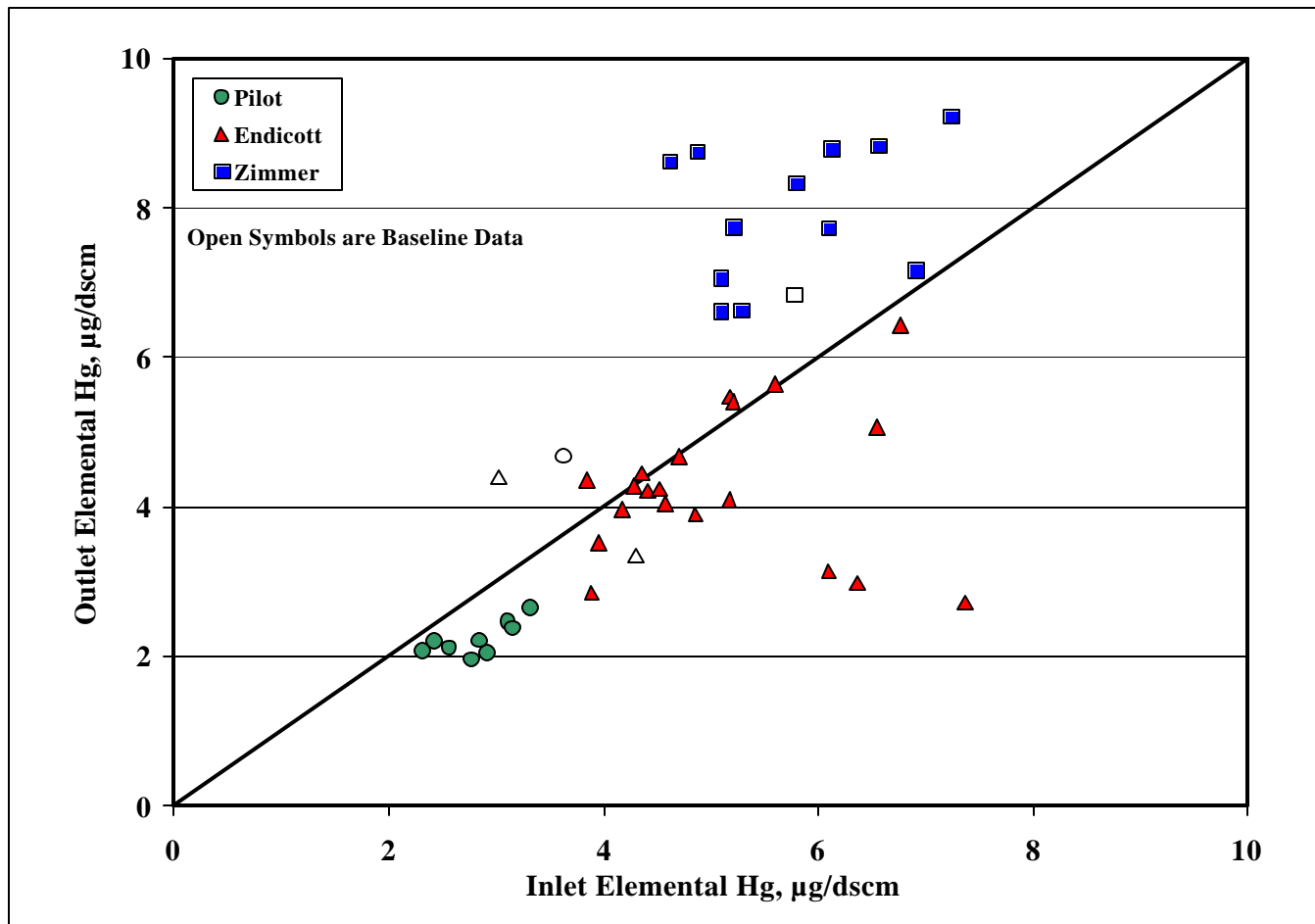


Fig. 17 Comparison of Scrubber Inlet and Outlet Elemental Mercury Concentration.

below the 45° line). However, the Zimmer data shows that the reagent had no effect in preventing the formation of elemental mercury in the scrubber so all of the data is above the 45° line. Additional pilot tests may be required to determine why Zimmer performed differently than the other tests both in the proportion of elemental mercury formed in the boiler and in the scrubber mercury removal performance with reagent injection.

Project Sponsors

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1. Munthe, et. al., "The Aqueous Reduction of Divalent Mercury by Sulfite", *Water, Air, and Soil Pollution* **56**: 621-630, 1991.